Spatial and Temporal Trends in Surface Water and Sediment Contamination in the Laurentian Great Lakes

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"Capsule": Contaminant levels in the Great Lakes have declined over the past 20 years; Lake Ontario remains most contaminated.

Abstract

Data from recent sediment and surface water surveys have been collated and mapped to illustrate the spatial distribution of contaminants across the entire Great Lakes basin. Information from historical surveys, together with data from surface water monitoring programs in three major connecting channels, has also been collated in order to evaluate temporal trends. In general, Lakes Superior and Michigan exhibited the lowest levels of sediment contamination while Lake Ontario had the highest. Contaminants such as ?-HCH (lindane) and dieldrin were ubiquitous in surface waters across the entire basin, which was indicative of atmospheric sources. The distribution of other compounds including hexachlorobenzene, octachlorostyrene and mirex indicated the presence of local sources within the watersheds of the connecting channels. Surficial sediment contamination was found to have decreased markedly since the late 1960s and 1970s. Similarly, surface water contamination decreased over the period 1986-1997 with concentrations of dieldrin, hexachlorobenzene, octachlorostyrene and mirex reduced by over 50%. However, the spatial distributions of both sediment and surface water contamination indicate that further effort is warranted in reducing local sources of contaminants, particularly in Lake Ontario.

1. Introduction

Agricultural, industrial and municipal activities, both within the Great Lakes basin and in upwind areas, have resulted in pollution by a variety of contaminants and the subsequent degradation of ecosystem health. Accumulation of pollutants in sediments, tissues of benthic invertebrates, and fish are the result of both historical and contemporary inputs. Information on the occurrence and spatial distribution of toxic substances in the Great Lakes furthers understanding of the role human activities play in discharging these chemicals to the environment, and can also serve as a benchmark in assessing contaminant discharge reduction strategies. These initiatives include the Great Lakes Water Quality Agreement and the Binational Toxics Strategy, which are collaborative processes by which all levels of government, environmental organizations, the public and industry work toward the goal of elimination of persistent toxic substances.

There is a considerable body of literature documenting the accumulation of persistent contaminants in the Great Lakes up until the period of the late 1960s through the mid-1970s. These intensive lake-wide sediment surveys detected the presence of compounds including PCBs (Frank et al., 1979, Frank et al., 1977), organochorine pesticides (Frank et al., 1977, Van Hove Holdrinet et al., 1978) and mercury (Cahill et al., 1981, Thomas, 1972, Thomas, 1974, Kemp and Thomas, 1976, Thomas and Jaquet, 1976) in lake sediments of all of the Laurentian Great Lakes at elevated concentrations due to the influence of anthropogenic activities. However, these studies pre-dated binational strategies to mitigate deleterious environmental impacts due to persistent toxics, including the banning of PCBs and the phasing-out of leaded gasoline. Studies using sediment cores have concluded that deposition rates for a number of persistent organic pollutants (POPs) in the Great Lakes generally peaked during the period 1960 – 1980, with rates decreasing after this time (Pearson et al., 1998, Wong et al., 1995, Schneider et al., 2001). However, these studies were generally

restricted to a small number of sample sites. Over the period 1994 – 2002, Environment Canada and its collaborating agencies conducted sediment surveys in each of the Great lakes, and Lake St. Clair, on a rotational basis to fulfill commitments under binational contaminant reduction initiatives, to ensure compliance with sediment quality guidelines, to evaluate spatial and temporal trends, and to identify emerging contaminant issues. Sediment sampling during these recent surveys was designed, in part, to enable comparison of contemporary sediment contamination with the results of Great Lakes surveys conducted over the period 1968 – 1975. Lake Michigan surficial sediment was collected from 1994 through 1996 as part of a joint effort by Great Lakes Environmental Research Laboratory/NOAA, U.S. EPA-ERL Duluth under the Environmental Monitoring and Assessment Program, and U.S. EPA Great Lakes National Program Office under the Lake Michigan Mass Balance Program.

Concurrent with this sediment assessment initiative, monitoring of surface water in the lower Great Lakes interconnecting channels (St. Clair, Niagara and St. Lawrence Rivers, Williams et al., 2000, Merriman, 1988) and in the open-water lake areas (Williams et al., 1998a, Williams et al., 1998b, Williams et al., 2001) has been conducted since 1986 to track inputs, outputs and in-lake concentrations of toxic chemicals. Both surface water and sediment samples were analyzed for all, or part, of a broad suite of contaminants including polychlorinated biphenyls (PCBs), metals, polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Detailed reports from sediment surveys in Lake Michigan (Rossmann, 2002), Lake Erie (Painter et al., 2001) and Lake Ontario (Marvin et al., 2002) have been published. In this paper, we present general information on spatial distributions for selected contaminants in surface waters and bottom sediments in the Great Lakes basin. Results are compared with those of previous surveys to allow assessment of temporal trends, and are also discussed

within the context of applicable sediment quality guidelines and surface water quality objectives.

2. Materials and Methods

2.1. Sample collection

Surficial sediment samples from Lakes Erie (1997), Ontario (1998), Superior (2000) and St. Clair (2000) were collected aboard the CCGS Limnos using a mini box core sampling procedure. Samples collected from these surveys consisted of fine-grained sediments classified as glacio-lacustrine clay, sand, silt or mud. The top 3 cm of the sediment was sub-sampled for analyses of persistent organic pollutants, metals, particle size, and nutrients. Detailed descriptions of sampling procedures and locations can be found in Marvin et al. (2002a,b) and Painter et al. (2001). Lake Michigan surficial sediments were collected using a box corer (preferred method) or Ponar dredge. The top 1 cm of the sample was sub-sampled for subsequent analyses. Detailed descriptions of sampling procedures and locations can be found in Rossmann (2002).

Water at the head (Fort Erie) and mouth (Niagara-on-the-Lake) of the Niagara River was collected using a large-volume 24-hour time-integrated dissolved/particulate phase sampling protocol under the auspices of the Niagara River Upstream/Downstream Program (Williams et al. 2001). Detailed descriptions of sampling protocols and analyses for contaminants have been detailed elsewhere (NLET, 1997, NRAP, 1992, NRSP, 1995). Open-lake surface water samples for Lakes Superior, Erie and Ontario were collected using a submersible pump (1m depth) and extracted on-board ship in dichloromethane using a large-volume continuous-flow Goulden extractor (Goulden and Anthony, 1985) and subsequently analyzed by gas chromatography – mass spectrometry. Detailed descriptions of sampling and analytical methods can be found in Stevens and Neilson (1989) and NLET (1997). Sampling

and analytical methods for the St. Clair River Water Quality Evaluation Program and the St. Lawrence River (Wolfe Island) Surface Water Monitoring Program were similar to those for the Niagara River Upstream/Downstream Program.

2.2. Analyses

Detailed descriptions of analyses for organic pollutants in sediments can be found in Painter et al. (2001) and Marvin et al. (2002a,b). Briefly, dried sediment samples were extracted in dichloromethane and subjected to an open-column Florisil cleanup procedure followed by analysis using gas chromatography with electron capture detection (GC/ECD). Details of analysis of Lake Michigan sediment for PCBs are described in Van Hoof and Hsieh (1997a and 1997b). Briefly, wet surficial sediments (20-40 g) were dried with sodium sulfate and extracted with dichloromethane. Extracts were cleaned up using columns containing 3% deactivated silica gel overlaid with 10% deactivated alumina and analyzed by GC/ECD. Total PCBs for sediments in Lakes Erie and Ontario were based on the sum total of 103 individual congeners and were not corrected for blanks or surrogate recoveries. Total PCBs for Lake Michigan sediments were based on the sum total of 110 individual congeners; total PCB concentrations less than 4 ng/g were blank-corrected. All analyses were subject to a rigorous QA/QC protocol including field replicates, laboratory duplicates, recovery surrogates and procedural blanks. For the Lake Erie and Lake Ontario PCB organic analyses, surrogate recoveries were typically >90%; procedural blanks and surrogate recoveries were evaluated against criteria established by Environment Canada from replicate analyses of standard reference materials over a two-year period. Field replicates were typically within 30%.

Trace metal and mercury analyses for surficial sediment surveys, with the exception of Lake Michigan, were performed by Caduceon Laboratories (Ottawa, ON). Briefly, trace metal concentrations were determined by a hot aqua-regia extraction with measurement by

ICP-AES (McLaren 1981). Total mercury was determined by digestion with hot nitric acid and hydrochloric acid followed with measurement by cold vapour atomic absorption spectrometer (USEPA 1981). A detailed description of the analysis of mercury in Lake Michigan sediments can be found in Rossmann (2002). Lake Michigan sediments were extracted by automated digestion (Leeman Labs, Inc. 1993), or microwave digestion (Uscinowicz and Rossmann 1997), and subsequently analyzed using an automated mercury analysis system (Leeman Labs, Inc. 1991). The automated mercury analysis system was based on cold vapour atomic absorption spectrophotometry. Analyses of trace metals in Lake Michigan sediments were performed by inductively-coupled plasma – mass spectrometry (ICP/MS) after microwave digestion in 10% v/v nitric acid.

3. Results and Discussion

3.1. Spatial Distributions and Temporal Trends in Surficial Sediment Contamination

The Great Lakes together with their interconnecting channels represent a water area of roughly 250,000 km^2 and a watershed land area of approximately 525,000 km^2. Sediments in the Great Lakes generally represent a primary sink for contaminants (Schneider et al., 2001), and can act as a source through resuspension and subsequent redistribution within the individual lakes. Surficial sediments, defined as the top 1-3 cm, represent the bulk of material available for resuspension. However, burial in sediments also represents a primary mechanism by which contaminants are sequestered and prevented from re-entering the water column. Based on ^{210}Pb dating of sections of sediment cores collected in offshore depositional areas during the surveys, data reported for surficial sediments generally correspond to the following dates of accumulation: Lake Superior, 1980 – 2000; Lake Michigan, 1990 – 1996; western basin of Lake Erie, 1995 – 1997; Lake Ontario, 1990 – 1998. With the exception of Lake Superior, data presented in this paper generally represent contaminant burdens accrued during the 1990s.

The spatial distribution of mercury in Great Lakes surficial sediment is shown in Figure 1. The lake-wide and basin-specific (where applicable) average concentrations for mercury, other selected metals and PCBs are shown in Table 1. The highest concentrations of mercury in sediments of Lakes Michigan, St. Clair, Erie and Ontario were observed in offshore depositional areas characterized by fine-grained sediments. The spatial distribution of mercury across the Great Lakes was generally representative of the distributions of the other metals, with the exception of lead, where the degree of contamination in Lake Michigan was similar to Lake Ontario. Contaminant concentrations are generally correlated with particle size, hence the distribution of mercury shown in Figure 1 is not only a function of loadings and proximity to sources, but of the influence of substrate type and bathymetry as well. The association of mercury with sediment type in Lakes Erie, Ontario and Michigan was previously reported (Thomas, 1972, Thomas and Jaquet, 1976, Rossmann, 2002); concentrations of mercury increased from shallow nearshore coarser sediments outwards into deep-water depositional basin sediments composed of silts and clays. According to Thomas (1974), the distribution of mercury throughout the Great Lakes in areas not significantly impacted by local sources is generally dictated by sedimentology; therefore, sedimentology is also a primary influence in the distribution of other contaminants as well.

The most recent sediment surveys of Lakes Superior, Huron, St. Clair, Erie and Ontario were not conducted to the same degree of spatial resolution as earlier surveys conducted over the period 1968 – 1972. However, the majority of stations sampled in Lakes Ontario, Erie, St. Clair and Huron during 1997 – 2002 were stations sampled by Environment Canada over the period 1968 – 1972; the sampling strategy in these historical surveys was based on grid intersections to avoid site-selection biases. The majority of samples from our recent surveys were comprised of fine-grained silts and clays, as we specifically targeted depositional sediments. Therefore, the lake-wide average concentrations and 75th percentile

values in Table 1 for these five lakes generally represent contamination in deep-water depositional areas. More intensive sampling in nearshore areas, which should be considered when making the inter-lake comparisons, may have influenced the Lake Michigan data set. For example, the Lake Michigan average total PCB concentration of 50 ± 48 ng/g represents both sites considered to be depositional in nature (80 ± 41 ng/g) and non-depositional (6.7 ± 7.7 ng/g). Contaminant concentrations corresponding to depositional basin sediments were generally normally distributed; therefore we have expressed the lake-wide averages as arithmetic means. This generally normal distribution is illustrated by PCB concentrations in Lake Ontario sediments, where the arithmetic mean (100 ng/g) was essentially the same as the median value (98 ng/g).

Mercury contamination was found to be generally quite low in Lakes Huron, Michigan and Superior, and higher in Lakes St. Clair, Ontario and the western basin of Lake Erie. There was an apparent spatial distribution in contamination in Lake Erie with decreasing concentrations from the western basin to the eastern basin, and from the southern area to the northern area of the central basin (Figure 1, Table 1). The spatial pattern in Lake Erie was influenced by industrial activities in the watersheds of major tributaries, including the Detroit River, and areas along the southern shoreline (Painter et al. 2001).

Mercury contamination in Lake Ontario was consistent among the three major depositional basins, as a result of the predominant circulation pattern that distributes particulate material around the lake in a counterclockwise fashion. Distributions of a variety of other contaminants in Lakes Erie and Ontario, including PCBs and organochlorine pesticides, were similar to that of mercury (Painter et al. 2001, Marvin et al., 2002a,b). The relatively higher mercury concentrations in Lake Ontario, compared to the other lakes, are reportedly the result of local historical sources (Diamond et al. 1993, Pirrone et al. 1998). Pirrone et al. (1998) reported that wastewater sources were the dominant source of mercury

in Lake Ontario over the period 1940 – 1970, but atmospheric sources were predominant after this period. Therefore, mercury contamination in Lake Ontario is primarily the result of historical loadings, combined with intra-lake mixing processes prior to deposition. Considering that atmospheric sources are now predominant, further decreases in mercury levels in Lake Ontario sediments are to be expected.

Mercury contamination in Lakes St. Clair and Erie resulted in commercial fishing bans in the late 1960s; implementation of these bans was a primary impetus behind the series of intensive sediment surveys conducted by Environment Canada during the late 1960s and early 1970s. In the 2000 survey on Lake St. Clair, the highest concentrations were observed in the central and east-central areas of the lake (Figure 1). The combination of this spatial pattern, which was similar to that determined by Thomas (1974) and Mudroch and Hill (1989), and the roughly five-fold higher lake-wide average concentration compared to Lake Huron (Table 1), indicated the presence of sources of mercury on the Canadian side of the St. Clair River due to chemical manufacturing.

A detailed discussion of mercury distributions and fluxes in Lake Michigan surficial sediments can be found in Rossmann (2002). Mercury concentrations in sediments collected over the period 1994 – 1996 were generally highest in the deep-water depositional basins and exhibited a spatial pattern that conformed to the lake's bathymetry. Results of an intensive sediment survey of Green Bay in 1987 – 1990 showed a higher degree of mercury contamination (average of 0.360 μg/g) than the open lake areas, which was attributed to historical contamination from pulp and paper industrial discharges (Rossmann and Edgington, 2000). The distribution of PCBs in the open lake areas of Lake Michigan (1994 – 1995) was similar to that of mercury in that the highest concentrations were associated with the depositional basins. Concentrations of total PCBs exceeding 100 ng/g were only found in the southern and central basin areas; concentrations exceeding 150 ng/g were only found in

the southern basin. The apparent differences in PCB content in sediments in the northern and southern basins in Lake Michigan contrast with the more consistent distribution observed for mercury. Source function differences, combined with differences in rates of burial for the two basins, could explain the disparate spatial distributions of PCBs versus mercury.

Low mercury levels in Lakes Superior (2000) and Huron (2002) did not result in definitive contaminant distributions (Figure 1). Mercury contamination in Lake Superior is attributed to a number of sources, including atmospheric deposition from mercury generated both outside and within the basin, and from direct discharges from industrial activities including mining, chlor-alkali production, and pulp and paper production (Rossmann, 2002). Estimates of loadings from atmospheric deposition of mercury originating outside the Lake Superior basin range from 38% (Rossmann, 1999) to 58% (Rolfhus et al., 2003). Although loadings to Lake Superior are generally attributed to anthropogenic sources, the distribution of mercury may be partially due to local natural sources as well. Sedimentary rocks can contain high burdens of mercury that can result in elevated concentrations in tributary and lakebed sediments (> 0.500 μg/g) in areas such as Thunder Bay (Painter et al., 1994); the highest mercury values in the Lake Superior survey (0.30 μg/g and 0.33 μg/g) were detected near Thunder Bay (Figure 1). Lake Huron exhibited the lowest degree of mercury contamination of all the lakes. Sediment mercury concentrations at most stations were roughly equivalent to background levels (0.025 μg/g); the background concentration was estimated from the deepest sections of benthos cores, the dates for which correspond to pre-colonial times.

For the purposes of this paper, we selected mercury as a focal point for discussion of spatial distributions and temporal trends in sediment contamination throughout the Great Lakes, which are related in turn to sources, sedimentology and bathymetry, and circulation patterns in the individual lakes. Mercury data for Great Lakes sediments represents our most

complete and current information. In addition, spatial distributions in mercury contamination generally represent those of other toxics, both other metals and organics such as PCBs, as accumulation of a broad range of contaminants on a lake-by-lake basis can be the result of common sources, e.g., chlor-alkali production. We previously published the results of studies of sediment contamination by a broad range of organic contaminants and metals in both Lakes Erie (Painter et al. 1999, Marvin et al. 2002) and Ontario (Marvin et al., 2002, Marvin et al., 2003). Concentrations of select contaminants in surficial sediments of Lakes Erie and Ontario are shown in Table 2. Data for Lake Erie sediments are also presented for the individual basins to illustrate the trend toward increasing concentrations from east to west for a number of contaminants including PCBs, dioxins and furans, mercury and hexachlorobenzene (HCB). Conversely, contaminant concentrations among the three major depositional basins in Lake Ontario are generally similar. Table 2 also shows background levels of metals in the two lakes represented by concentrations in the deepest sections of benthos core samples that generally pre-date industrial activity. Therefore, the ratios of surficial to background metal concentrations reflect the impact of anthropogenic activity.

Comparisons with data from historical surveys conducted during the period 1968 to 1975 show a general decrease in sediment concentrations for a wide variety of contaminant classes throughout the Great Lakes. Surveys conducted in Lake Erie in 1997 (Painter et al. 2001) and Lake Ontario in 1998 (Marvin et al. 2002b) showed that surficial sediment PCB concentrations have declined roughly three-fold and six-fold, respectively, in the last thirty years. Concentrations of mercury and lead in Lake Ontario surficial sediments declined from 0.79 µg/g and 125 µg/g, respectively, in 1968 to 0.59 µg/g and 69 µg/g, respectively in 1998 (Marvin et al. 2002b). In 1971, the Lake Erie surficial sediment 75th percentiles for mercury in the western, central and eastern basins were 1.72 µg/g, 0.58 µg/g and 0.65 µg/g, respectively, while the corresponding values in 1997 were 0.65 µg/g, 0.25 µg/g and 0.09

μg/g. However, sediments in Lake Ontario were more contaminated, compared to Lake Erie,

and continued to exceed sediment quality guideline values for a number of contaminant

classes (Marvin et al. 2002a).

Rossmann (2002) reported a decrease in mercury concentrations in Lake Superior

sediments between 1969 and 1994; the rate of decrease between 1969 and 1981 was 10

ng/g/year and between 1981 and 1994 was 3.8 ng/g/year. The rate of decrease for mercury in

Lake Ontario sediments, using data from Marvin et al. (2002b) was estimated to be roughly 7

ng/g/year. Lake-wide average surficial sediment mercury concentrations in Lakes St. Clair

(0.20 μg/g) and Huron (0.04 μg/g) also represent substantial declines from corresponding

values in Lake St. Clair in 1970 (0.63 μg/g, Thomas et al., 1976) and Lake Huron in 1969

(0.22 μg/g, Thomas, 1973). The lake-wide average mercury concentration for Lake Superior

(0.09 μg/g) in 2000 was the same as the value for a 1973 survey (0.09 μg/g, Thomas, 1974),

however, sediments collected in the 2000 Lake Superior survey represent accumulation over

roughly a 20-year time period from 1980 – 2000, while sediments from the other lakes

represent accumulation during the period 1990 – 1998. Therefore, sampling of Lake Superior

at higher resolution than the top 3 cm would be required to better estimate trends in mercury

contamination over the past 30 years. Based on the comparison of lake-wide average

sediment mercury concentrations from our most recent surveys with historical surveys, we

estimate reductions in mercury contamination over the last three decades to range from

approximately 25% for Lake Ontario to 80% for Lake Huron.

Some historical information does not fit well within the context of current levels of

contamination determined using our most recent data sets. Frank et al. (1981) calculated a

mean total PCB concentration of 17.3 ng/g (N=92) for sediments in the depositional basins of

Lake Michigan, a value that is significantly lower than the 80 ng/g value resulting from the

1994 – 1995 samples for the same sediment types. In considering the 1979 North American

ban on PCBs, and subsequent decreases in PCB loadings to the Great Lakes, reductions in surficial sediment PCBs were expected. General comparisons of the 1994 – 1995 Lake Michigan data with other studies (Swackhamer and Armstrong, 1988, Hermanson et al., 1991, Golden, 1994) resulted in a more credible temporal trend. Although total PCBs in the southern and central basin areas appear to have increased or remained unchanged, contamination in the northern basin appears to have declined significantly (40%) since 1984. The lack of reductions in PCBs in the southern basin may be the result of focusing processes and redistribution of PCBs, and/or the continuing influence of sources. As discussed previously, comparisons of PCB data from recent surveys in Lakes Erie and Ontario compare favorably with those of the historical surveys conducted by Frank et al. (1977, 1979), in that there have been significant reductions in contamination as a result of reduced loadings. However, direct comparisons in contaminant concentrations may be substantially influenced by differences in sampling protocols (e.g., Shipek dredge vs. mini box core) and/or analytical methods (e.g., total Aroclor PCBs determined using packed-column GC vs. total congener PCBs determined using capillary GC). These differences in methodologies were discussed by Oliver et al. (1989), in comparing results of a 1981 study with data from Frank et al. (1979) for Lake Ontario.

The determination of spatial distributions and temporal trends in sediment contamination also can assist in identification and assessment of contributions of primary sources of contaminants. A discussion of these trends in sediment mercury contamination illustrates this point. Sediments in Lakes Michigan and Superior generally exhibited low levels of contamination, with the exception of lead in sediments of Lake Michigan (lake-wide average of 141 μg/g), which exhibited roughly the same degree of contamination as the western basin of Lake Erie (average of 161 μg/g). There appeared to be no significant transport of contaminants to Lake Huron from Lakes Michigan and Superior, as evidenced by

most concentrations of metals in surficial sediments being similar to estimated background levels or geochemical norms. Sources and loadings of mercury to Lake Huron appear to have been reduced to the point that no apparent spatial pattern exists. Historical studies had indicated that mercury contamination in Saginaw Bay and Georgian Bay were sources of mercury to southern Lake Huron and Lake St. Clair (Thomas, 1974). Our most recent studies indicate that these source areas are no longer significant.

As in the historical studies, elevated concentrations of mercury were found in the central and east-central areas of Lake St. Clair (2000), the western basin of Lake Erie (1997 – 1998), and the three major depositional basins of Lake Ontario (1998). The current degree of contamination in these areas is substantially lower than peak levels that occurred in the mid – 1950s through the early 1970s. However, the similarity in spatial patterns between recent and historical surveys indicates significant sources within the individual lake basins continue to influence contaminant distributions over large areas. Areas of the major connecting channels including the Niagara, lower Detroit and upper St. Clair Rivers are all associated with historical mercury cell chlor-alkali production; these areas were also intensively industrialized and were primary sources of a variety of persistent toxics to the open lakes, including PCBs. Localized areas of highly contaminated sediment, and/or hazardous waste sites associated with these industrial historical sources, may continue to act as sources of these contaminants and influence their spatial distributions. Conversely, these local sources may no longer be predominant, and the spatial patterns observed in our most recent surveys may reflect resuspension, intra-lake mixing and deposition of existing sediment inventories. In this case, further declines would be expected as these contaminants are ultimately deposited and buried in the sedimentary record.

A particularly interesting deviation from the spatial patterns observed in the historical surveys relates to the relatively low contaminant levels found in sediments of the eastern

basin of Lake Erie in 1997 – 1998. Thomas and Jaquet (1976) and Frank et al. (1977) found elevated levels of PCBs and mercury in the eastern basin, which were attributed to transport of sediment-bound contaminants from the western basin along the southern shore subsequent to deposition. Our recent survey found no evidence of significant circulation of contaminants from west to east in Lake Erie; in the case of metals, current levels of contamination in the eastern basin are similar to background concentrations estimated from the deepest sections of benthos core samples (Table 2). We are unable to determine the exact cause of the discrepancy between the 1997 – 1998 and 1971 data sets; however, our re-evaluation of the Frank et al. and Thomas and Jaquet data sets suggests that contamination in the eastern basin originally attributed to loadings in the western basin could have been the result of local sources. Oliver and Bourbonniere (1985) estimated that the Detroit River was the source of only one-third of the PCBs in the central and eastern basins of Lake Erie, while two-thirds had other sources. Townsend (1998) has documented the presence of hazardous waste facilities along the New York State shoreline of southeastern Lake Erie, and their subsequent remediation under the United States Superfund Program. Other factors may have included the reduced sampling intensity in 1997 – 1998 (N=68) vs. 1971 (N=258), or changes in sediment transport processes. However, based on well-established reductions in contaminant loadings to Lake Erie, elimination of local sources provides the most rational explanation for the relatively low levels of contamination in the eastern basin.

Surficial sediment concentrations were not only compared with historical levels, but were also assessed against guideline values established for the protection of aquatic biota. We have selected the Canadian Sediment Quality Guidelines Probable Effect Level (PEL, CCME, 1999) as a benchmark. These guidelines can be applied as screening tools in the assessment of potential risk, and for the determination of relative sediment quality concerns. A comparison of Canadian and U.S. sediment quality guidelines and their application can be

found in Rheaume et al. (2000). For the five metals and PCBs (Table 1), PEL guideline

exceedances were frequent in Lake Ontario for lead, cadmium and zinc. Guideline

exceedances were rare in all of the other lakes, with the exception of lead in Lake Michigan

where the PEL (91.3 µg/g) was exceeded at over half of the sites. There were no PEL (277

ng/g total PCBs) guideline exceedances for PCBs in any of the Great Lakes sediments

included in our data set. We have also developed a sediment quality index (SQI) that

produces a numerical score based on the frequency and magnitude of sediment guideline

exceedances. Relative sediment quality scores for Lakes Erie and Ontario reflected the

general spatial distributions shown for the mercury and dieldrin in Figures 1 and 2,

respectively; Lake Ontario exhibited relatively poorer sediment quality, compared to Lake

Erie (Marvin et al., 2003b). The poorer sediment quality in Lake Ontario was attributed to

generally higher levels of contamination for a broad range of compounds.

3.2. Spatial Distributions and Temporal Trends in Surface Water Contamination

Spatial distributions and temporal trends in contaminants in Great Lakes surface

waters were assessed both through large-volume water sampling during open-lake surveys,

and from monitoring activities in three major interconnecting channels (Niagara River, St.

Clair River, St. Lawrence River at Wolfe Island). Open-lake surface water cruises were

conducted during the period 1992-2000 on a rotational basis in Lakes Superior (1997), Erie

(1994/1995/2000) and Ontario (1992/1993/1999). An overview of trends in organic

contaminants in open-water areas of Lakes Erie, Ontario and Superior over the period 1992 –

1996 can be found in Williams et al. (2001), while detailed assessments of spatial

distributions and temporal trends in surface waters of Lake Erie (1994/1995) and Lake

Ontario (1992/1993) can be found in Williams et al. (1998a, 1998b). Connecting channel

monitoring to assess trends in concentrations and loadings in contaminants over time has

been ongoing since 1986. Both the open-lake surveillance and connecting channel

monitoring studies encompass a broad suite of POPs including organochlorine pesticides (OCs) and PCBs, chlorobenzenes, polycyclic aromatic hydrocarbons (PAHs) and industrial by-product chemicals. Method detection limits for OCs and PCBs in the dissolved phase for open-water surveillance over the period 1992 – 1996 ranged from 0.01 ng/L for aldrin to 0.81 ng/L for total PCBs. In general, concentrations of most contaminants in surface waters approached, or were below, the analytical method detection limits. Only a small number of OCs were routinely detected in all three lakes (Erie, Ontario and Superior); dieldrin, a-HCH, ?-HCH (lindane) and heptachlor epoxide. Other ubiquitous compounds included the current-use herbicides atrazine and metolachlor. Concentrations of suspended particulates in these lakes were typically very low, which precluded the production of reliable particulate phase data. Therefore, the current emphasis of the open-lake surveillance program is on the determination of dissolved phase contaminant concentrations with adequate spatial coverage, rather than both particulate and dissolved phase data from a limited number of stations. As a result, the most compelling spatial distribution and temporal trend information for persistent toxics in open lake areas are represented by the dissolved phase concentrations of a small number of OCs. PCBs were also ubiquitous in all three lakes; however, some data did not meet quality assurance and quality control criteria and is not reported. Anderson et al. (1999) have reported total PCB data for surface waters of the Great Lakes sampled in spring, 1993.

Spring surface water (1m) dissolved phase concentrations of dieldrin in the Great Lakes, and the temporal trend expressed as the annual mean concentrations in the interconnecting channels, are shown in Figure 2. Data shown in Figure 2 are the result of surveys conducted over the period 1997 – 2000, and represent our most current surface water data. Concentrations of dieldrin in Lakes Superior (lake-wide average 0.11 ng/L) and Huron (0.04 ng/L) were lower, compared with Lakes Erie (0.21 ng/L) and Ontario (0.18 ng/L). Current loadings of dieldrin to Lakes Superior and Huron are due to atmospheric deposition.

The relatively higher concentrations in the lower lakes are the result of a combination of sources, including historical usage in the watersheds, loadings from the upstream lakes and connecting channels, and atmospheric deposition. There was a spatial distribution of dieldrin observed in Lake Erie (Figure 2); concentrations decreased from the western basin (basin-wide average 0.42 ng/L) to the central (0.16 ng/L) and eastern (0.16 ng/L) basins. This spatial distribution is attributed to loadings from upstream entering Lake Erie via the Detroit River, and loadings via tributaries characterized by agricultural watersheds in which dieldrin was historically heavily used, e.g., Maumee River. The spatial distribution of lindane in Lake Erie has previously been observed to be similar to that shown for dieldrin, however, lake-wide average spring concentrations of lindane in Lakes Superior (1997, 0.38 ng/L), Erie (1998, 0.32 ng/L) and Ontario (1992, 0.24 ng/L) were generally similar (Williams et al., 2001). In the case of α-HCH, the lake-wide mean concentration in Lake Superior in spring 1997 (2.8 ng/L) was substantially higher than Lake Erie (spring 1998, 0.41 ng/L) and Lake Ontario (spring 1998, 0.40 ng/L). These inter-lake comparisons are consistent with the ubiquity of these compounds in the global atmosphere, with the result that atmospheric deposition represents the primary source throughout the Great Lakes. The relatively high concentration of α-HCH in Lake Superior can be attributed to its greater surface area, which results in correspondingly greater loads of atmospherically derived contaminants. Contaminants in the Lake Superior water column can then undergo prolonged periods of recycling due to the cold water temperatures and low sedimentation rates (Swackhamer et al., 1999, Jeremiason et al., 1998). The most recent basin-wide surface water PCB data were published by Anderson et al. (1999), who reported a range of total PCB concentrations from 100 pg/L in Lake Superior to 1.6 ng/L in the western basin of Lake Erie. Lake Superior also exhibited the lowest lake-wide average total PCB concentration, while Lakes Michigan and Ontario were highest.

The interpretation of temporal trends in contaminants associated with surface waters in open lake areas is complemented by monitoring programs in several of the major connecting channels; sites at upstream/downstream locations in the St. Clair and Niagara Rivers, and at Wolfe Island in the St. Lawrence River, have been sampled on a continual basis over the past two decades. These programs were designed to investigate trends in toxics in the major rivers as a means of assessing the efficacy of control measures to reduce discharges. These programs can also elucidate changes and trends in both concentrations and loads over time, and assist in the identification of probable sources, both local and regional, through comparison of upstream/downstream concentrations. In addition, the identification of temporal trends in the rivers can be used to substantiate the interpretation of data from the open lake surveillance programs. The annual mean recombined whole water concentrations (i.e., dissolved + particulate) of dieldrin at both Fort Erie and Niagara-on-the-Lake showed distinct downward trends over the period 1986 – 1997 (Figure 2). Concentrations of dieldrin and lindane declined by roughly 50% during this period. Data from the upstream/downstream stations in the St. Clair River and a monitoring station at Wolfe Island in the St. Lawrence River showed a similar trend (Figure 2). Weekly data for recombined whole water dieldrin concentrations in surface water samples at Niagara-on-the-Lake over the period 1986 – 1997 are shown in Figure 3. Both dieldrin and lindane are associated primarily with the dissolved phase (>90%). Compounds primarily or exclusively particulate-bound, such as mirex and octachlorostyrene (OCS), exhibited decreases of 50% and 90%, respectively, at Niagara-on-the-Lake during the period 1986 – 1997. In general, concentrations of chlorobenzenes, organochlorine pesticides and PCBs (reduction of 72%) at Fort Erie and Niagara-on-the-Lake have decreased markedly since 1986. Table 3 shows the changes in annual mean concentrations and loads in both the dissolved and particulate phases

for selected compounds at the Niagara River upstream/downstream stations between 1986 and 1997.

The ubiquity of compounds such as lindane and dieldrin in surface waters throughout the Great Lakes, and the similarity in concentrations detected at both the upstream and downstream sites in the connecting channels, implicated atmospheric deposition as the primary source, and did not indicate the presence of local sources. Elevated levels of both lindane and dieldrin in the western basin of Lake Erie, compared to the central and eastern basins, indicated potential local sources of these compounds, however, this spatial trend was not apparent in all surveys. In contrast to compounds such as dieldrin and lindane, spatial patterns and connecting channel upstream/downstream comparisons for other compounds strongly indicated the presence of significant local sources, i.e., some contaminants were prevalent in most samples at the downstream station, but were not detected or rarely detected at the upstream station. Spatial patterns in HCB and OCS were indicative of sources in the St. Clair River, while the Niagara River was implicated as a source of HCB, OCS and mirex. For example, the average whole water HCB concentration over the period 1990-1997 downstream in the Niagara River at Niagara-on-the-Lake (0.095 ng/L) was roughly four-fold higher than the corresponding upstream concentration at Fort Erie (0.025 ng/L). Trends in loadings and concentrations can also reflect general trends in usage patterns, and application, e.g., agricultural pesticides. Concentrations and loadings of the current-use herbicide metolachlor at both Fort Erie and Niagara-on-the-Lake more than doubled over the period 1989 – 1997, while applications on field corn and soybeans in Ontario in 1983, 1988, 1993 and 1998 were approximately 817,000 Kg, 1,630,000 Kg, 1,290,000 Kg and 1,330,000 Kg, respectively (Hunter and McGee, 1999), i.e., metolachlor usage in these applications was 60% higher in 1998, compared to 1983.

The quality of surface water, both in the open lakes and within the connecting channels, was also assessed against New York State ambient water quality standards for the protection of human consumers of fish (NYSDEC, 1998). These standards represent the most sensitive criteria among the agencies mandated with monitoring water quality in the lower Great Lakes. Despite the significant improvements in surface water quality, concentrations of several contaminants at both Fort Erie and Niagara-on-the-Lake, including PCBs and dieldrin, still regularly exceeded the New York State standard. Total DDT and OCS exceeded the standard in 80% and 20%, respectively, of the samples at Niagara-on-the-Lake; lindane concentrations in both the open-lake and connecting channels were typically one-tenth or less of the New York State standard. The latest United States EPA water quality criterion for total PCBs (USEPA, 2002) is 64 pg/L, which is below the range of concentrations in the Great Lakes (100 pg/L to 1,600 pg/L) reported by Anderson et al. (1999).

4. Conclusions

Spatial distributions and temporal trends in both surficial sediments and surface waters indicate progress in the reduction of persistent toxics in the Great Lakes basin. Since the implementation of the ban on PCBs in 1979, surficial sediment concentrations have declined to a point that we have not observed exceedances of the Canadian PEL guideline within the open-lake depositional areas of any of the Great Lakes. Reductions in sediment PCB contamination in Lakes Erie and Ontario were estimated at roughly 70% and 80%, respectively, based on comparisons of lake-wide average concentrations from surveys in the late-1990s with surveys conducted in the late 1960s through the early 1970s. These conclusions are supported by the results of other studies in which core profiles were used to assess contaminant accumulation rates, inventories, and reductions in loadings over the past several decades (e.g., Wong et al., 1995, Pearson et al., 1997, Schneider et al., 2001).

Comparisons of the degree of improvement in sediment quality assessed using surficial sediments vs. core profiles are difficult. Sediment core studies are site-specific, while comparisons of data from surficial sediment studies conducted over several decades may be influenced by differences in analytical and sampling methods. However, the results of these studies are complementary in that reductions in concentrations of many contaminants have been concluded to be substantial. These conclusions are also in concurrence with assessments of reductions in sources of toxics in North America as reported through initiatives including the Great Lakes Binational Toxics Strategy; in the case of mercury, source reductions in Canada and the United States currently stand at approximately 80% and 40%, respectively (GLBTS, 2002). Ultimately, corresponding reductions in contaminant concentrations in both surface waters and sediments of the Great Lakes are anticipated, but at rates that are subject to factors including physical processes within lakes, and regional/global influences.

Relatively higher sediment contaminant concentrations, compared to other areas within the same lake, or compared to the other lakes, indicated local sources of some contaminants as in the case of Lake Ontario. Spatial trends in sediment contamination may have been influenced by industrial activities in the watersheds and along major tributaries; contaminants originating within tributary watersheds or even derived through atmospheric deposition, can ultimately be deposited in deep water areas. This process is sometimes referred to as sediment focusing (Rossmann, 2002). In concert with the general reductions in surficial sediment contamination, concentrations of contaminants in surface waters, both in the open lakes and the connecting channels, have declined. Using data from the Niagara River Upstream/Downstream program, we estimate that concentrations and loadings of most persistent toxics in surface waters have dropped roughly 60% since 1986. However, despite the substantial overall decrease in surface water contamination, concentrations of some

toxics, such as PCBs, still exceed some water quality criteria. As with the spatial distributions in sediment contamination, spatial distributions in surface water contamination provided evidence as to primary sources. Similar concentrations and the ubiquity of lindane and dieldrin indicated atmospheric deposition as the primary source, while differences in concentrations at upstream and downstream stations in the connecting channels indicated local sources of HCB, OCS and mirex. These local sources, although their effects have been reduced, still result in active loadings of some contaminants to the open lake environments.

Management actions such as bans (e.g., PCBs and mirex) and phasing out of leaded gasoline have undoubtedly been the primary contributors to the marked declines in contamination by a number of compounds. Other actions have presumably contributed to the general declines in both surface waters and sediments, including the remediation of sites of contaminated sediments, reduction and/or elimination of discharges from hazardous waste facilities, reduction of open-lake disposal of contaminated sediments, and reductions in loadings from atmospheric sources. A thorough review of atmospheric deposition of toxics to the Great Lakes can be found in Hoff et al. (1996).

Acknowledgements

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Figure Legends

Figure 1. Surficial sediment total mercury concentrations (μg/g dry wt.) in the Great Lakes. The Canadian Sediment Quality threshold effect level (TEL) is 0.174 μg/g and the probable effect level (PEL) is 0.486 μg/g.

Figure 2. Spatial distribution of dieldrin in surface water (dissolved phase in ng/L), and annual mean concentrations (ng/L) in the interconnecting channels from 1986 to 1998 (whole water in ng/L). Water surveys were conducted in Lake Superior (1997), Lake Huron (2000), Lake Erie (1998) and Lake Ontario (1999).

Figure 3. Recombined whole water dieldrin concentrations[1] in surface water samples collected weekly at Niagara-on-the-Lake at the mouth of the Niagara River from 1986 to 1997. Data from Williams et al. (2000). [1]Apparent zeroes are due to missing dissolved phase concentrations.

Mercury ppm

Legend
- 0.000 - 0.100
- 0.100 - 0.170
- 0.170 - 0.486
- 0.486 - 1.000
- 1.000 +

Niagara-on-the-Lake

ng/L
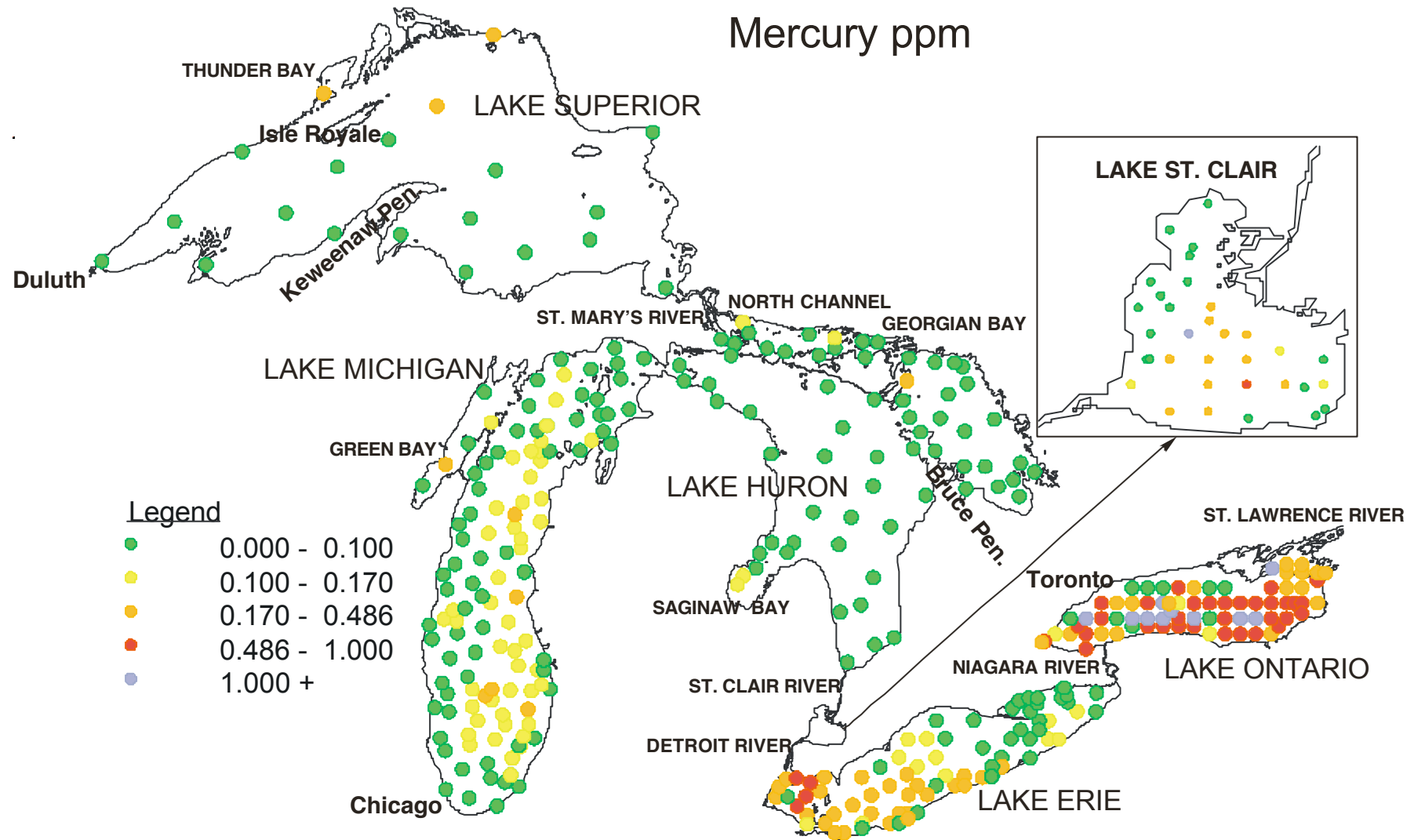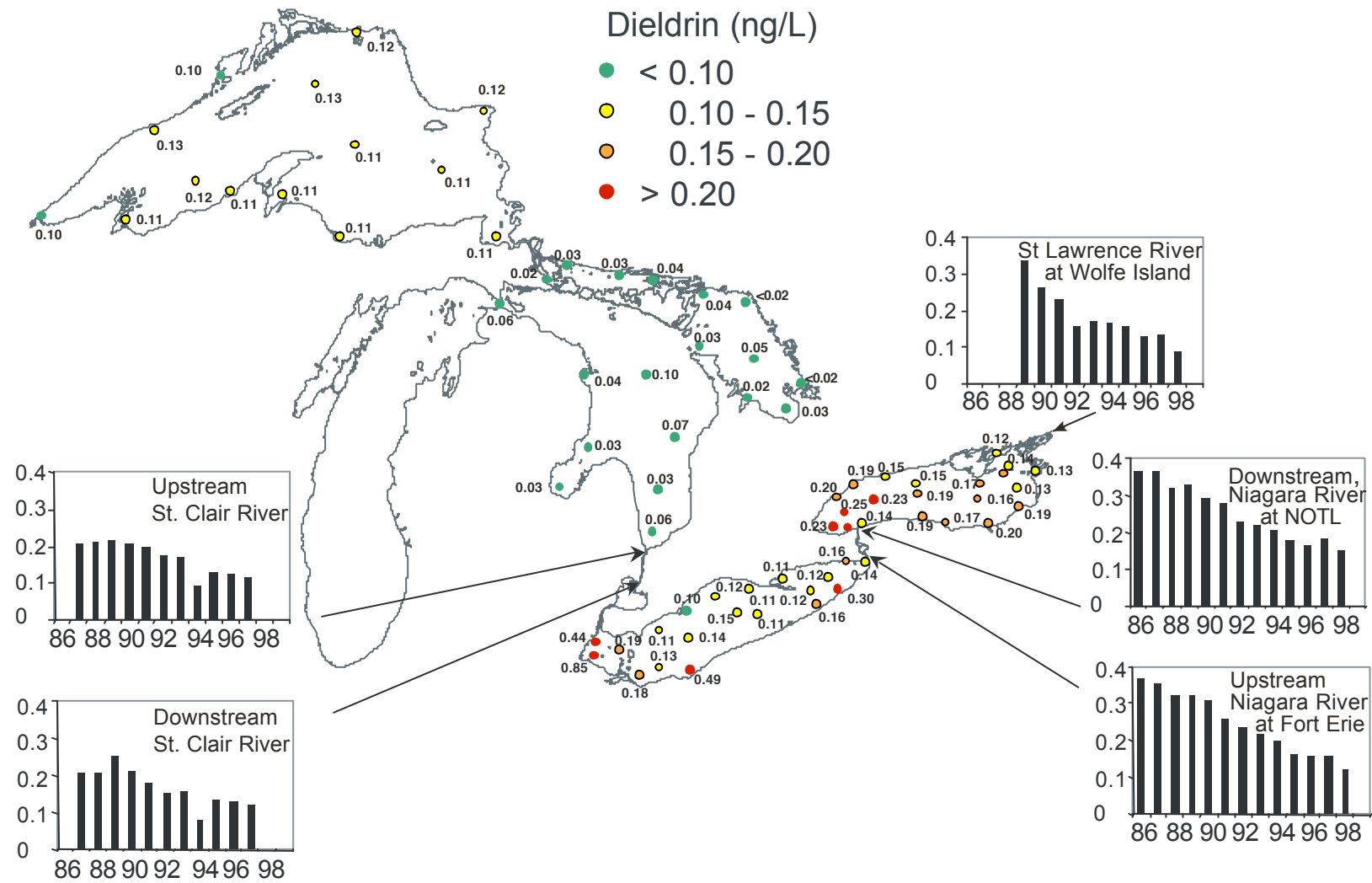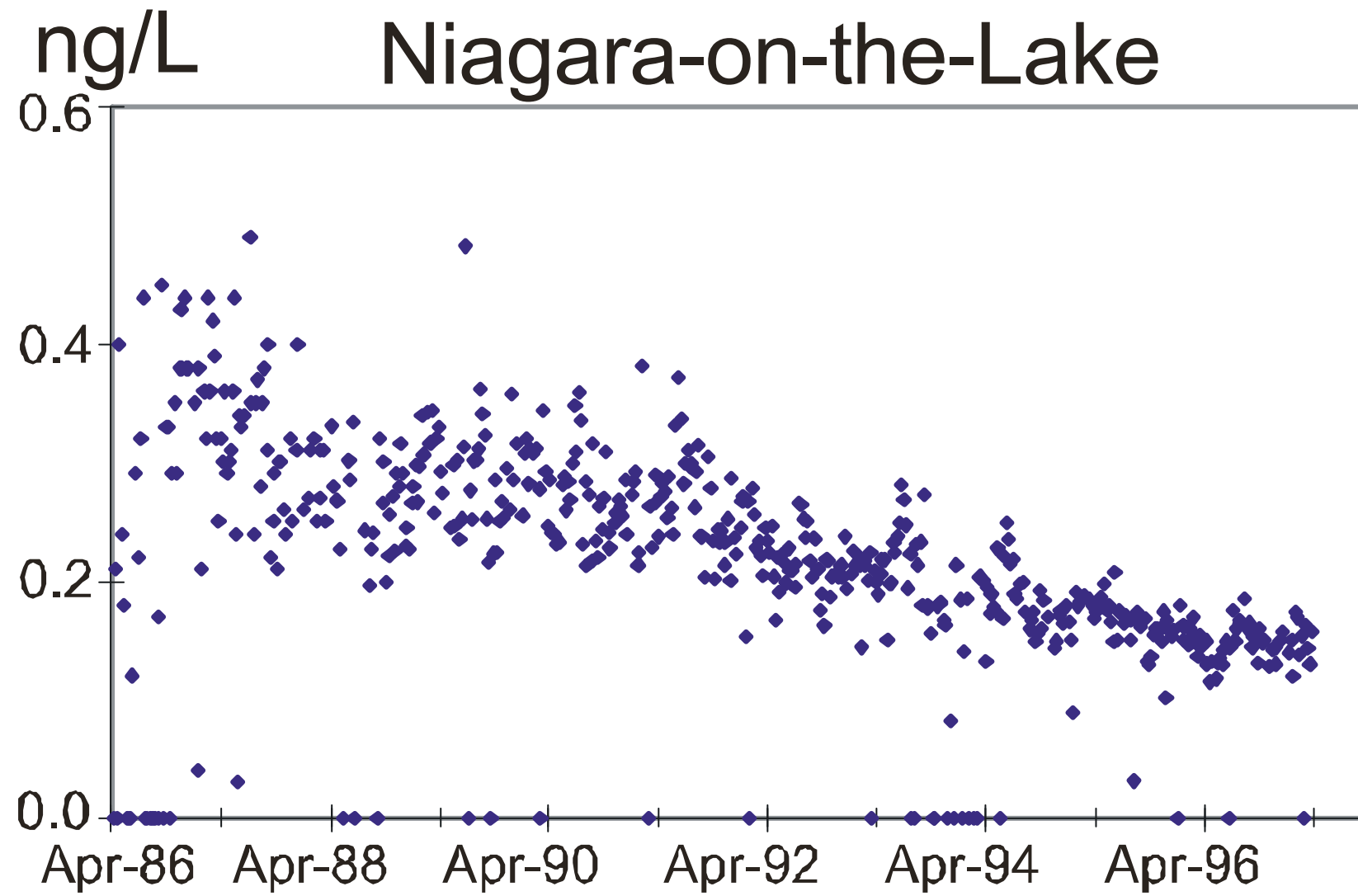
List of Tables.

Table 1. Great Lakes lake-wide average contaminant sediment concentrations (μg/g), minimum and maximum concentrations, Canadian Sediment Quality Guidelines Probable Effect Levels (CCME, 1999), and percentages of sites exceeding PEL guidelines. ND denotes not detected, NA denotes not available.

Table 2. Lake Erie and Lake Ontario background sediment contaminant concentrations, surficial sediment basin-specific 75th percentiles, and Lake Erie basin-specific average and Lake Ontario lake-wide average concentrations. Background concentrations were estimated from concentrations corresponding to the deepest sections of benthos cores. Some data presented taken was taken from Marvin et al. (2002).

Table 3. Changes in concentrations and loadings of contaminants at the inflow of the Niagara River at Fort Erie, and at the outflow of the Niagara River at Niagara-on-the-Lake for the period 1986 – 1997. All data taken from Williams et al. (2000) for dissolved or particulate phases for which sufficient data was available for trend analysis. Mean annual concentrations and loads were calculated using the Maximum Likelihood Estimation (MLE) method (Williams et al., 2000).

Table 1. Great Lakes lake-wide averages (μg/g), Canadian Sediment Quality Guidelines and percentages of sites exceeding guidelines (ND denotes not detected, NA denotes not available)

		Cadmium	Copper	Lead	Zinc	Mercury	PCBs(ng/g)
Canadian Sediment Quality Guidelines PEL (CCME 1999)		3.53	196.60	91.30	314.80	0.486	277.00
Superior	Lake-wide Average	ND	98	47	105	0.088	NA
	% Exceeding PEL	0	5	5	0	0	
	Minimum	0	2.3	5.8	10	0	
	Maximum	0	215	95	175	0.328	
Michigan	Lake-wide Average	1.5	31	67	140	0.077	47
	% Exceeding PEL	5	0	38	6	0	0
	Minimum	0.009	0	0	1.5	0.002	0
	Maximum	7.8	82	185	400	0.264	220
Huron	Lake-wide Average	0.33	32	34	92	0.043	NA
	% Exceeding PEL	0	0	6	0	0	
	Minimum	0	0.85	0.95	8.3	0.01	
	Maximum	2.8	86	120	240	0.37	
St.Clair	Lake-wide Average	ND	11.6	7.74	41	0.196	NA
	% Exceeding PEL	0	0	0	0	6	
	Minimum	ND	3.7	0	17	0.014	
	Maximum	ND	20	29	85	1.19	
Ontario	Lake-wide Average	1.8	59	72	260	0.586	100
	% Exceeding PEL	17	0	38	35	62	0
	Minimum	0	3.7	5.2	11.2	0	2.6
	Maximum	5.8	110	200	1,300	1.4	255
Erie	Lake-wide Average	1.2	36	41	161	0.187	98
	% Exceeding PEL	3	0	1	1	6	0
	Minimum	0	3.1	4.4	24	0.006	1.9
	Maximum	4.4	68	105	320	0.940	245
	Western Basin	1.4	41	44	175	0.402	161
	Central Basin	1.4	38	46	175	0.167	97
	Eastern Basin	0.45	27	22	112	0.069	36

Table 2.

Chemical	Background Concentration				75th Percentile				Average			
	West Erie	Center Erie	East Erie	Ontario	West Erie	Center Erie	East Erie	Ontario	West Erie	Center Erie	East Erie	Ontario
Cadmium (μg/g)	<1	<1	<1	<1	1.6	2.0	1.0	3.3	1.4	1.4	0.45	1.8
Chromium (μg/g)	22	31	27	27	55	47	33	54	49	46	26	43
Copper (μg/g)	15	35	28	50	47	49	34	86	41	38	27	59
Lead (μg/g)	13	23	19	15	57	60	32	110	44	46	22	72
Mercury (μg/g)	0.034	0.049	0.042	0.04	0.65	0.25	0.09	0.79	0.402	0.167	0.069	0.187
Nickel (μg/g)	28	46	36	43	50	52	40	77	39	42	32	55
Zinc (μg/g)	64	110	96	100	210	240	150	360	170	180	110	260
Total PCBs (ng/g)					180	110	48	140	160	100	36	100
Dioxins & Furans (pg/g TEQs)					33	23	2	175	28	16	1.8	101
p,p'- DDT (ng/g)					6.2	1.7	1.3	4.8	4.1	1.3	1.2	3.8
Dieldrin (ng/g)					0.84	1.1	0.69	2.0	0.84	0.76	0.54	1.4
Hexachlorobezene (ng/g)					5.9	1.6	1.3	40	3.8	1.2	0.79	23

Table 3.

Chemical	Period of Record	Fort Erie				Niagara-on-the-Lake			
		% Conc. Change		% Load Change		% Conc. Change		% Load Change	
		Diss.	Part.	Diss.	Part.	Diss.	Part.	Diss.	Part.
Organics									
Metolachlor	1989-1997	+110	--	+130	--	+110	--	+130	--
Hexachlorobenzene	1986-1997	--	--	--	--	-70	-51	-67	-64
a-HCH	1986-1997	-84	--	-85	--	-80	-68	-83	-76
?-HCH (lindane)	1986-1997	-56	--	-61	--	-52	--	-57	--
p,p'-DDT	1986-1997	--	-42	--	-76	--	-35	--	-52
Dieldrin	1986-1997	-59	-38	-63	-74	-57	-60	-62	-70
Heptachlor-epoxide	1986-1997	-57	--	-62	--	-56	--	-61	--
Mirex	1986-1997	--	--	--	--	--	-50	--	-63
PCBs	1986-1997	-59	-60	-63	-83	-59	-76	-64	-82
Octachlorostyrene	1989-1997	--	--	--	--	--	-90	--	-84
Metals		Whole Water % Conc. Change		Whole Water % Load Change		Whole Water % Conc. Change		Whole Water % Load Change	
Lead	1986-1997	-84		-86		-69		-72	
Mercury	1986-1997	-84		-86		-76		-79	
Cadmium	1986-1997	-48		-54		-44		-51	